

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: : Date: September 29, 2003
WHITE, Lloyd Steven et al. : Group Art Unit: 1764
Serial No.: 09/784,898 : Examiner: GRIFFIN, W.D.
Filed: February 16, 2001 : Docket No.: W9494-01
For: MEMBRANE SEPARATION FOR SULFUR REDUCTION

DECLARATION UNDER 37 CFR 1.132

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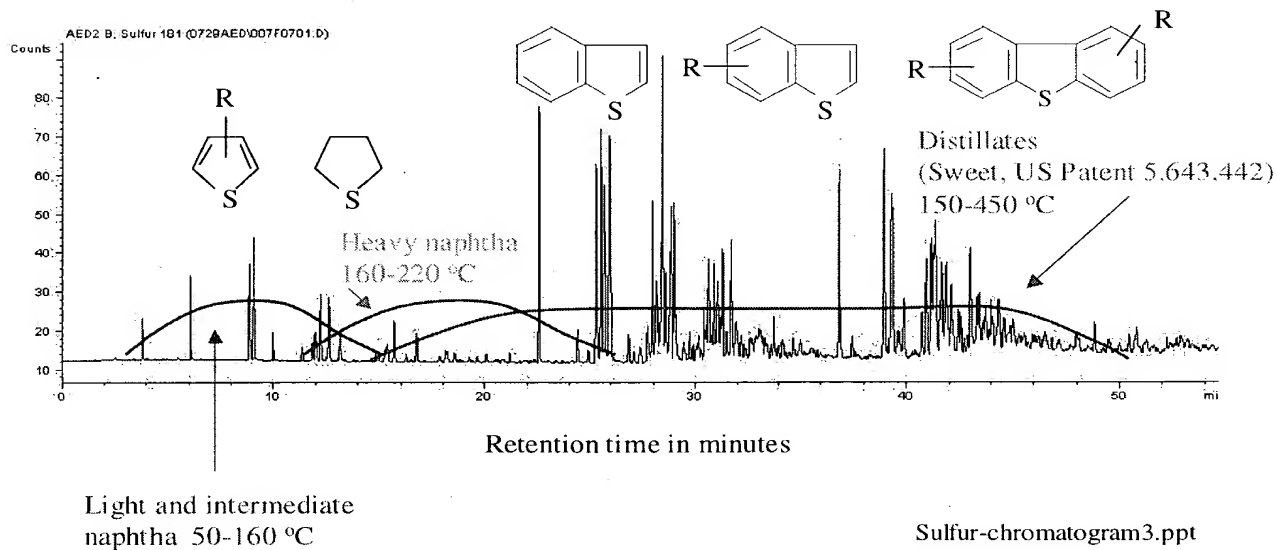
I, Lloyd S. White, hereby declares as follows:

1. I received my Ph.D. in organic chemistry from Cornell University in 1985.
2. From 1984 to 1989, I worked with the research division of UOP/Allied Signal on membrane separations in refinery applications.
3. I joined W.R. Grace & Co.-Conn. in 1989 and continued to work on refinery applications for membrane separations in natural gas purification, aromatics recovery and oil dewaxing processes.
4. I am currently employed with W.R. Grace & Co.-Conn. as a Principal Scientist in the FCC/Membrane Division.
5. I am a named author on at least 9 published papers in the area of membrane technology.
6. I am listed as an inventor on 8 issued U.S. Patents.
7. I am one of the inventors on U.S. Patent Application Serial No. 09/784,898.
8. I am familiar with the contents of the above-mentioned patent application.

9. To demonstrate the chemical differences in hydrocarbon petroleum fractions, I show the difference in the sulfur species present in various petroleum fractions. Figure 1 shows a typical chromatogram of a hydrocarbon feed used in refining processes. This chromatogram was supplied by the FCC Evaluation & Analytical group of Grace Davison and shows all of the sulfur compounds typically present in the naphtha to distillates range for hydrocarbon feeds. The method uses a gas chromatograph (GC) to split the individual hydrocarbon components in the naphtha and distillate ranges essentially by boiling point. The equipment is fitted with an atomic emission detector (AED) tuned for sulfur compounds. The x-axis shows the retention time in minutes of the sulfur compounds within the GC, while the y-axis shows the counts detected for each peak by AED, corresponding to concentration of compounds.

Figure 1

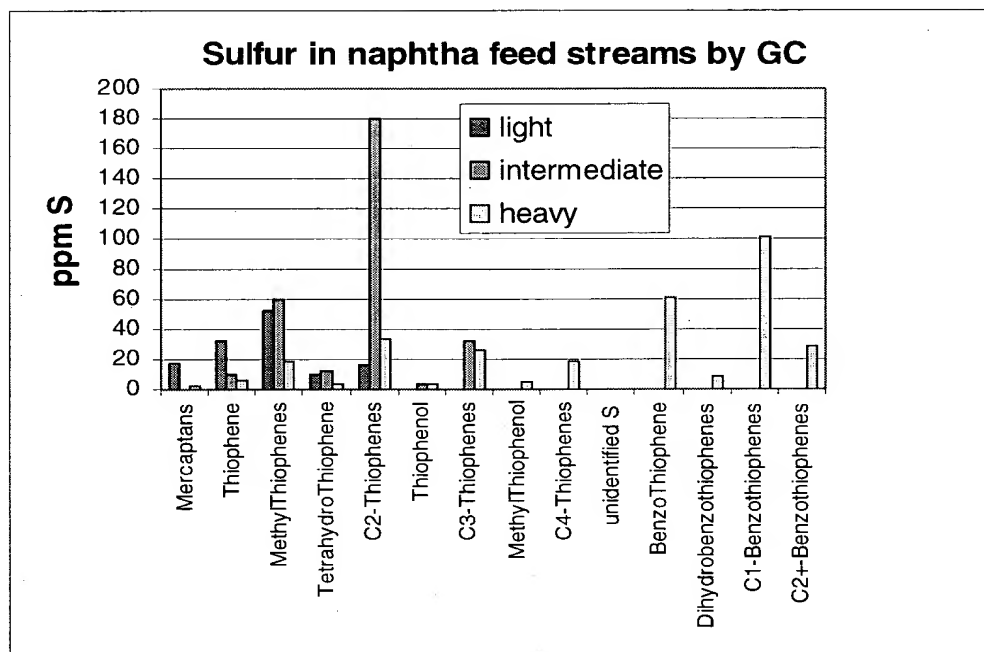
Typical chromatogram of sulfur compounds in hydrocarbon feeds.



As shown in Figure 1, the petroleum feed is separated into distillation fractions having different boiling point ranges. The first fraction includes light and intermediate naphthas having a boiling point range of 50-160 °C. The second fraction is a heavy naphtha having a boiling range of 160-220 °C. The third fraction include distillates described in Sweet (U.S. Patent 5,643,442) having a boiling point range of 150-450 °C. As shown in Figure 1, a key distinction in the composition of the petroleum fractions is the chemical composition of sulfur species present in the fraction. For example, the naphtha fractions (having a boiling range from 50-220°C) typically contain one ring aromatic and non-aromatic sulfur compounds while the distillate fractions as described in the Sweet et al. patent contain predominately two rings and higher aromatic sulfur compounds, such as benzothiophenes and higher alkyl benzothiophenes. As shown in Figure 1, benzothiophene has a boiling point of 221°C, and a retention time of just over 22 minutes. Thus, a naphtha sample truly cut at or below 220 °C will contain substantially no benzothiophene. However, since actual heavy naphtha samples can and do tail into higher temperatures, some benzothiophene and alkylbenzothiophenes can be present in heavy naphtha samples.

10. To demonstrate that the chemical composition can vary between fractions within the naphtha range, the distribution of sulfur compounds within the naphtha fractions obtained from a petroleum feed was analyzed using GC as described hereinabove. As shown in Figure 2 , the compositions of a light cat naphtha (LCN), an intermediate cat naphtha (ICN), and a heavy cat naphtha (HCN) was reported. Figure 2 shows that LCN has methylthiophenes as the major component, ICN has C2-thiophenes as the major components, while the HCN is dominated by compounds not present in the other two ranges (C4-thiophenes, benzothiophene, C1-benzothiophenes, and C2+-benzothiophenes). Therefore, the composition of light naphtha, intermediate naphtha and heavy naphtha feeds would also be chemically different.

Figure 2



11. To demonstrate that the ability of a membrane to remove sulfur is dependent upon the chemical composition of the sulfur species to be removed, a HCN was run in a laboratory experiment as described in USSN 09/784,898 at page 11, lines 18-27, with the exception that the experiment was ran at a 4% stage cut and the membrane was a polyurea-urethane membrane. The polyurea/urethane membrane produced a permeate stream from the feed stream of HCN. The results of the test are reported in Table 1. Note that a number of the compounds present in substantial concentrations in HCN have an EF (Enrichment Factor) less than the preferred EF of 1.5 or greater described in the application. In contrast, the two major sulfur compounds present in LCN and ICN have EF of 4.8 (methylthiophenes) and 2.6 (C2-thiophenes).

Table 1
Heavy Cat Naptha Pervaporation Trial

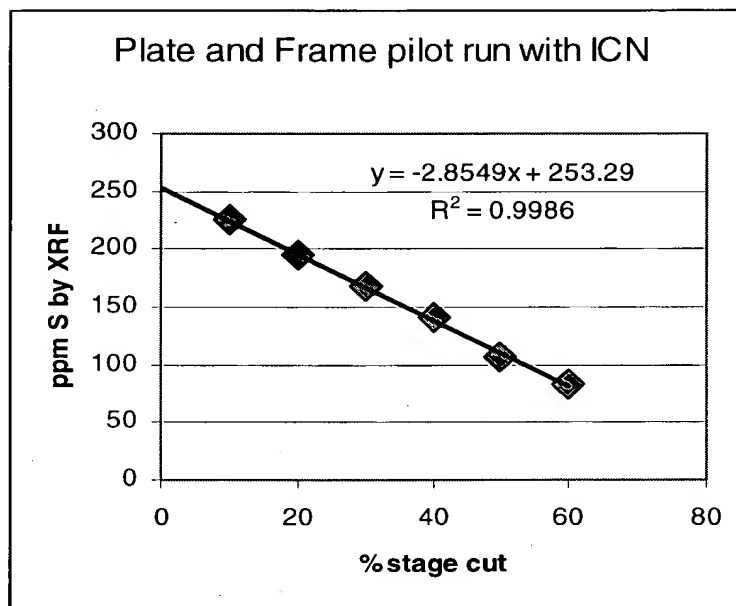
Test conditions:

Feed temperature at 109 °C, feed pressure 4.6 bar, and vacuum 1 mm Hg.

Reference 18644	141-1	141-2	
All ppm Sulfur	Feed	Permeate	EF
Mercaptans	3.1	27.1	8.72
Thiophene	6.1	40.2	6.64
MethylThiophenes	18.8	90.5	4.82
TetrahydroThiophene	3.7	8.1	2.17
C2-Thiophenes	34.2	87.4	2.56
Thiophenol	3.2	4.5	1.39
C3-Thiophenes	25.6	35.0	1.36
MethylThiophenol	4.7	5.3	1.13
C4-Thiophenes	18.4	12.1	0.65
Unidentified S in the Gasoline Range	0.0	1.1	NA
Benzothiophene	61.4	111.5	1.81
Dihydrobenzothiophenes	8.6	9.5	1.11
C1-Benzothiophenes	101.0	81.0	0.80
C2+-Benzothiophenes	28.3	4.6	0.16
Total Sulfur by GC	317.0	517.7	1.63

In practice, stage cuts are likely to be greater than 10%, such as described in example 7 of the application where stage cut is 30%. I report in Figure 3 the sulfur levels for a large stage cut experiment with a plate and frame module using ICN.

Figure 3



What was observed with ICN is that the reduction in sulfur levels was linear with stage cut up to 60%. The best fit line shows an excellent statistical correlation (R^2) of better than 99%. Also, note that sulfur levels have been reduced to below 100 ppm S for ICN even with a membrane that was less selective than used for the HCN experiment in Table 1. Given the observation that sulfur removal is linear with stage cut, one can then calculate what stage cuts are required in order to achieve less than 100 ppm S. I therefore calculated in Table 2 the performance of an HCN membrane system at large stage cuts based on the total sulfur EF determined with the data presented in Table 1 for 4% stage cut. Note that even at 90% stage cut, Table 2 shows that a polyurea-urethane membrane was unable to reduce the sulfur content of an HCN to the required level of less than 100 ppm S.

Table 2

Calculated values for sulfur removal and olefin retention at high stage cuts from heavy cat naphtha based on experiment reported in Table 1.

Stage cut (%)	Retentate sulfur (ppm S)	Olefin retention (%)
0	317.0	100.0
10	297.0	87.3
20	277.1	75.2
30	257.1	63.7
40	237.1	52.8
50	217.1	42.5
60	197.2	32.8
70	177.2	23.7
80	157.2	15.2
90	137.3	7.3

12. To demonstrate the sulfur content (ppm) and the olefins concentration (weight %) of LCN, ICN, and HCN previously shown in Figure 2, total sulfur EF for LCN, ICN, and HCN was calculated as a weighted average of the individual sulfur compounds determined for HCN. Note that the calculated EF for HCN equals the experimental value since that data is used as the basis for the calculation. Based on these calculated EF's, the sulfur removal rates are shown in Table 3. Because LCN and ICN have different sulfur compounds than HCN, it is possible to rapidly reduce sulfur levels in light and intermediate naphthas compared to HCN. For the membrane process shown earlier with HCN, LCN is calculated to be reduced to less than 30 ppm S at less than 20% stage cut, and ICN to less than 100 ppm S at less than 40% stage cut. Olefin retentions for these two cases are estimated at 75% for LCN and 53% for ICN.

Table 3

Calculated values for sulfur removal and olefin retention at high stage cuts from light and intermediate cat naphtha.

Stage cut (%)	LCN		ICN	
	Retentate sulfur (ppm S)	Olefin retention (%)	Retentate Sulfur (ppm S)	Olefin retention (%)
0	128.2	100.0	299.6	100.0
10	72.7	87.3	240.3	87.3
20	17.2	75.2	181.0	75.2
30			121.6	63.7
40			62.3	52.8

13. The results of these experiment indicate that there is a chemical difference is in the composition of distillates and naphtha petroleum fractions, and even in the different naphtha fractions themselves. A key difference being the chemical composition of sulfur species present in the hydrocarbons fractions. The naphtha ranges consists predominantly of alkyl substituted one-ring sulfur compounds, such as methyl-thiophene, while distillate fractions consists predominantly of 2-ring and higher alkyl substituted sulfur compounds, such as methyl-benzothiophene.
14. The above results further indicate that the ability of a membrane to remove sulfur is dependent upon the chemical composition of sulfur compounds in the fraction and therefore the chemical composition of the petroleum fraction itself.
15. The above results also show that LCN and ICN can be reduced to less than 100 ppm S using a polyurea-urethane membrane, while a polyurea-urethane membrane is not effective to reduce the sulfur content of an HCN to less than 100 ppm S.
16. Further, the above result indicate that a polyurea-urethane membrane can achieve an olefin retention of greater than 50% with both light and intermediate naphthas, while also reducing sulfur content to less than 100 ppm S.

I further declare that all statement made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

November 24, 2003

Date

Lloyd Steven White

Lloyd Steven White